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Assessment of the contribution from wood burning to the PM10 aerosol in Flanders, Belgium

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HIGHLIGHTS

► A one-year study with 7 sampling sites and a total of 644 daily PM10 samples.
► PM10 mass, elemental carbon, organic carbon (OC), and 3 anhydrosugars determined.
► Wood burning in Flanders appears to be a regional scale phenomenon.
► Wood burning is an important contributor to the PM10 OC and PM10 mass in winter.
► Less wood burning would help in complying with the European air quality legislation.

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ABSTRACT

From February 2010 to February 2011 PM10 aerosol samples were simultaneously taken every 4th day at 7 monitoring sites in Flanders, Belgium. Two of the sites (i.e., Borgerhout and Gent) were urban background sites; one (i.e., Mechelen) a suburban background site, and the other four (i.e., Hamme, Lier, Retie, and Houtem) rural background sites, whereby Hamme and Lier were expected to be particularly impacted by biomass burning. The samplings were done for 24 h and 47-mm diameter Pallflex® Tissuquartz™ 2500 QAT-UP filters were used. After sampling the PM10 mass concentration was determined by weighing; organic and elemental carbon (OC and EC) were measured by thermal–optical transmission analysis and the wood burning tracers levoglucosan, mannosan, and galactosan were determined by means of gas chromatography/mass spectrometry. The atmospheric concentrations of levoglucosan and the other two monosaccharide anhydrides showed a very clear seasonal variation at each site, with highest levels in winter, followed by autumn, spring, and summer. The levoglucosan levels for 5 of our 7 sites (i.e., Retie, Lier, Mechelen, Borgerhout, and Gent) were very highly correlated with each other (all between site correlation coefficients $r>0.9$, except for one value of 0.86) and the levels in the parallel samples of these 5 sites were similar, indicating that wood burning at these 5 sites was a regional phenomenon and that it was taking place in many individual houses on similar occasions (e.g., on cold days, weekends or holidays). The levoglucosan levels at Houtem and the correlation coefficients of the 5 sites with Houtem were lower, which is explained by the fact that the latter site is at less than 20 km from the North Sea so that the air there is often diluted by rather clean westerly maritime air. A peculiar behavior was seen for Hamme, with on many occasions very high levoglucosan levels, which was attributed to the fact that there is wood burning going on in several houses nearby this site. From our levoglucosan/mannosan ratios we derived the relative contributions of softwood and hardwood burning, thereby following the same approach as used by Schmidl et al. (Atmos Environ 2008;38:126–41). It was found that softwood burning accounted, on average, for about 70%, and there was little variation in this percentage with site or with season. The levoglucosan data were used to assess the contribution of wood burning to the OC and to the PM10 mass, again following the approach of Schmidl et al. (2008). The annual average contributions of wood burning OC to the PM10 OC were in the range of 20–25% for 6 of our 7 sites and 36% for Hamme; the averages for summer were 2.0–3.9% for the 6 sites and 14.5% for Hamme; the corresponding data for winter were 36–43% and 60%. As to the contribution from wood burning to the PM10 mass, the annual averages were in the range of 4.8–6.3% for 6 of our 7 sites and 13.3% at Hamme; the averages for summer were 0.51–1.14% for the 6 sites

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and 5.0% for Hamme; the corresponding data for winter were 8.6–11.3% and 22%. Our finding that wood burning is an important contributor to the OC and the PM10 mass, especially in winter, is in line with published data from various other sites in other European countries.

1. Introduction

Many studies have indicated that wood combustion and various other forms of biomass burning may provide a substantial contribution to the atmospheric particulate matter (PM) levels. In the industrialized world, including North America, Europe, and the Far East, wood is burned in fireplaces and wood stoves for different purposes, including pleasure, heating, and cooking. When prices of oil and natural gas rise, there is a tendency for increased usage of wood for heating and cooking purposes, which results in increased PM levels, as was, for example, the case for rural areas in the Czech Republic (Váňa et al., 2007). Wood burning in the industrial world is enhanced in winter, and in urban areas of southern California it was found to be responsible for 20–30% of the ambient fine particle mass concentration in that season in the 1980s (Schauer et al., 1996). As far as Europe is concerned, studies on the contribution from wood smoke to the PM have been carried out in several countries and in several environments, varying from Swiss Alpine valleys (e.g., Szidat et al., 2007) over rural background sites along a West–east transect in Europe (Puxbaum et al., 2007) to suburban and urban sites in countries like Norway (Yttri et al., 2005, 2009), Austria (Caseiro et al., 2009), the Czech Republic (Křůmal et al., 2010), and Italy (Piazzalunga et al., 2011). In most of the cited studies, levoglucosan was used as marker for wood burning. The use of levoglucosan as a tracer for biomass burning was introduced by Simoneit et al. (1999). Levoglucosan (1,6-anhydro-β-D-glucopyranose, $C_6H_{10}O_5$) arises from the pyrolysis of cellulose, the main building material of wood, at temperatures higher than 300 °C (Simoneit et al., 1999). Levoglucosan is accompanied by other minor stereoisomeric monosaccharide anhydrides in atmospheric aerosols, with mannosan (1,6-anhydro-β-D-mannopyranose) and galactosan (1,6-anhydro-β-D-galactopyranose) being the most important ones (Simoneit et al., 1999; Nolte et al., 2001). The latter compounds result from the pyrolysis of hemicelluloses, although the emitted amounts are substantially lower than those of levoglucosan. According to Locker (1988), levoglucosan is stable in the atmosphere, showing no decay over 8 h exposure to ambient conditions and sunlight. Fraser and Lakshmanan (2000) studied the acid-catalyzed hydrolysis of levoglucosan under atmospheric conditions and found no degradation within 10 days even under very acidic conditions. This finding was later confirmed by a study of Simoneit et al. (2004). In recent years, however, Hoffmann et al. (2010) and Hennigan et al. (2010) have published cautionary articles on the stability of levoglucosan, especially at high OH levels and under high relative humidity conditions. Such conditions may be quite important for biomass burning particles in tropical areas and during long-range aerosol transport, but are expected to be of minor importance for our study in Belgium, where the levoglucosan originates mainly from rather nearby sources.

The first use of levoglucosan for assessing the impact of wood smoke on PM in Europe was made by Zdráhal et al. (2002). For PM10 samples collected in a 1998 winter campaign at an urban background site in Gent, Belgium, 35% of the aerosol organic carbon (OC) was attributed, on average, to wood burning. Using the same approach as used for the winter data to the 1998 summer campaign data of Zdráhal et al. (2002), one arrives at an average summer contribution from wood burning to the OC of 4.9%. In a follow-up study, Pashynska et al. (2002) measured levoglucosan and OC in PM10 samples collected during 2000–2001 winter and 2001 summer campaigns at the same site in Gent. Based on their data, and using the same approach as in Zdráhal et al. (2002), one arrives at average contributions from wood smoke to the OC of 38% and 3.1% for the winter and summer samples, respectively. These old data suggest that wood burning has a substantially larger impact on the PM in Belgium in winter than in summer. As the old studies were restricted to one single site in Belgium and the number of samples was quite limited (10 or less per campaign), the Flemish Environment Agency felt that a more extensive study, including several sites and involving many more samples per site was at order. In the current study PM10 samples were taken every 4th day from February 2010 to February 2011 at 7 different sites spread over Flanders, Belgium. The aims of the current study were to examine to what extent the results of Zdráhal et al. (2002) and of Pashynska et al. (2002) could be substantiated, to investigate the seasonal variation in the impact from biomass burning to the OC and PM mass, and to assess the relative contributions from hardwood and softwood combustion to the wood smoke. Whereas use was made of levoglucocan in fine particle emissions from fireplace combustion of woods in the northeastern United States, as obtained by Fine et al. (2001), for assessing the contribution from wood burning in the approach used in Zdráhal et al. (2002), it was felt that recent source data obtained for Austrian wood stoves by Schmidl et al. (2008) would be more appropriate for the source apportionment in the current study. In addition to the aims indicated above, the new study had also environmental policy and regulatory aspects in mind. According to the 1st daughter directive of the European Commission (Council Directive 1999/30/EC) the daily PM10 mass concentration of 50 μg/m^3 cannot be exceeded more than 35 times per calendar year at any given location. In Belgium there are several PM10 monitoring sites where there are difficulties complying with this regulation (Maenhaut, 2007). It is therefore of interest to investigate the causes of the possible exceedances in order to be able to take appropriate measures. Taking into account that the exceedances occur mostly in winter, when the impact from wood burning is expected to be largest, data on the contribution from wood smoke to the PM10 mass in that season are of great value for environmental policy makers.

2. Experimental

2.1. Sampling sites and aerosol collections

The 7 sampling sites where the aerosol collections were done are shown in Fig. 1. Two of the sites (i.e., Borgerhout, which is within the city of Antwerpen, and Gent) are urban background sites; Mechelen is a suburban background site, and the other 4 sites (Hamme, Lier, Retie, and Houtem) are rural background sites, although the latter is quite a relative concept in a densely populated and industrialised region as Flanders. Hamme and Lier were expected to be particularly impacted by biomass burning. In Hamme, the sampler was placed in a rural area with individual houses; in the neighborhood of the site are several inhabitants who use wood as fuel. At Lier there were within a radius of 1 km two horticulture farms that used wood as fuel, but it appeared in the course of the project that one of the two farms had just stopped its activities before the start of the project. 24-h PM10 aerosol samples (with filter changing at 23:55 UT) were simultaneously taken every 4th day at the 7 sites from 6 February 2010 to 7 February 2011. Leckel SEQ 47/50 low-volume samplers operating at 2.3 m^3/h and 47-mm diameter Pallflex® Tissuquartz™ 2500 QAT-UP (prefired in the factory) quartz fiber filters were used. The exposed area of the filter during sampling (aerosol deposit area) was 11.64 cm^2 and the air volume for each sample was 55.1 m^3. Consequently, the sampling face velocity was 54.8 cm/s. A total of 92 actual samples were taken at each site; also 9

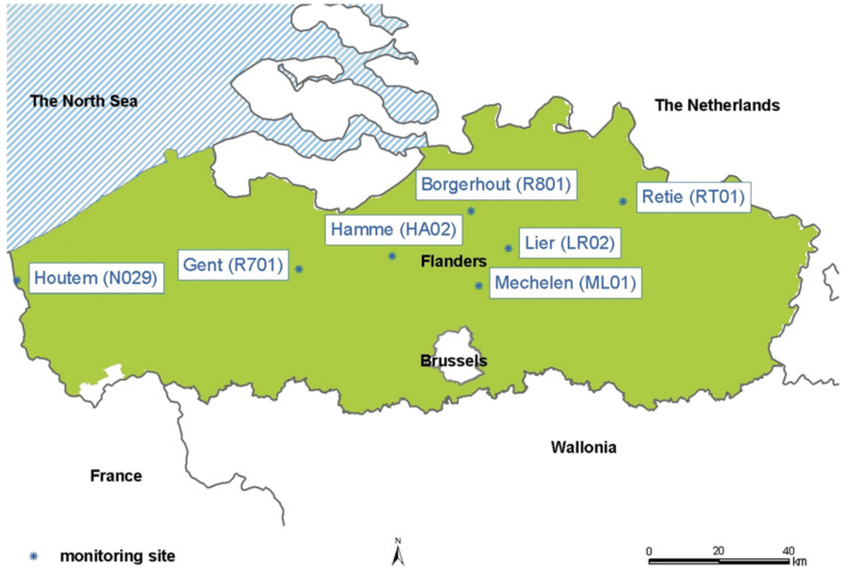

Fig. 1. Location of the 7 sampling sites. The labels in parentheses are site codes, as used by the Flemish Environment Agency.

field blanks were taken at each site; no air was drawn through the field blanks. The actual samples and field blanks were stored in the freezer below −18 °C until analysis.

2.2. PM mass measurement and analysis for carbonaceous components

After sampling, the PM10 mass concentration was determined by dual weighing of the filters according to the more stringent PM2.5 European reference method EN 14907 (2005). Both the actual samples and the field blanks were weighed and the PM10 mass data for the actual samples were corrected for the net masses obtained with the field blanks. The average field blank value for the PM10 mass was 1.09 μg/m^3. Filter punches were taken for chemical analysis, which were stored at −18 or −25 °C until analysis. One punch (of 1.5 cm^2) was used for the determination of organic, elemental, and total carbon (OC, EC, and TC) by thermal–optical analysis using the NIOSH temperature protocol (Birch and Cary, 1996; Maenhaut et al., 2009) and light transmission (TOT) and reflectance (TOR) were simultaneously monitored. It is noted that the NIOSH protocol provides lower EC data than various other temperature protocols, as was, for example, already found by Schmid et al. (2001). The data for the actual samples were corrected for the data obtained for the field blanks The field blank values were around 0.8 μg/m^3 for OC and TC and <0.1 μg/m^3 for EC. The TOT data were retained for further analysis. The comparison of the TOT and TOR data has been discussed elsewhere (Maenhaut et al., 2011); the TOR/TOT ratio for EC was site-dependent, with the median ratio (over the whole year) ranging from 1.4 for Borgerhout to 2.0 for Hamme. A detailed description of the uncertainties associated with the OC, EC, and TC measurements is given by Viana et al. (2006). The uncertainty is made up of a constant part (which is 0.2 μg C/cm^2 for OC and EC and 0.3 μg C/cm^2 for TC) and of a variable part which amounts to 5% of the OC, EC or TC mass loading.

2.3. Analysis for monosaccharide anhydrides

A 1.0 cm^2 filter punch of each actual sample and field blank was subjected to analysis for levoglucosan, mannosan, and galactosan (L, M, and G). The analyses were performed by means of gas chromatography/mass spectrometry (GC/MS) after extraction and trimethylsilylation, using the method described in Pashynska et al. (2002), but the extraction was now done with methanol instead of with dichloromethane–methanol (80:20, v/v), use was made of a different recovery standard, and a slightly modified GC temperature program was employed. Pashynska et al. (2002) compared the extraction yields of the monosaccharide anhydrides (and also glucose) for pure dichloromethane, dichloromethane–methanol (80:20, v/v), and pure methanol. They found that dichloromethane–methanol (80:20, v/v) was as efficient as methanol and they decided therefore to retain dichloromethane–methanol (80:20, v/v) for the further measurements. Considering that we often measure additional polar compounds in our aerosol samples, for which methanol provides higher extraction yields than dichloromethane does, we typically use pure methanol in our GC/MS analyses of samples since 2002 (e.g., Ion et al., 2005). The recovery standard in the present work was methyl O-L-xylanopyranoside (mXP). The GC temperature program was as follows: initial temperature of 100 °C, which is maintained during 2 min, followed by a gradient of 5 °C min^{-1} to 180 °C, then followed by a gradient of 20 °C min^{-1} to 310 °C, after which this last temperature is maintained during 2 min. The total GC/MS analysis time is 26.5 min. The retention times of the analytes are approximately as follows: L, 17.94 min; M, 17.48 min; G, 17.01 min; and mXP, 17.34 min. For the quantification of the monosaccharide anhydrides calibration curves of about 10 points were made. A typical GC/MS total ion current chromatogram is shown in Fig. 2. This chromatogram was obtained for the sample that was collected on 23 February 2010 in Hamme. The figure shows that all analytes and the internal recovery standard are separated down to the baseline. The precision (1 relative standard deviation) of our method for the individual monosaccharide anhydrides in the aerosol filter samples is estimated to be between 5 and 10%. The blank-free detection limit for levoglucosan

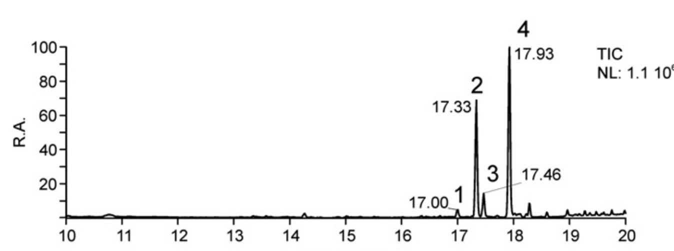

Fig. 2. Total ion current chromatogram [relative abundance (R.A.) versus time] obtained for the sample that was collected on 23 February 2010 in Hamme. The numbered peaks are for the following compounds: 1: galactosan; 2: mXP; 3: mannosan; and 4: levoglucosan. Abbreviation: NL, normalization level.

for the analysis of our filters (using a punch of 1.0 cm^2) is 0.02 ng/m^3. The data for the actual samples were corrected for the field blanks. The field blank value was around 0.7 ng/m^3 for levoglucosan and below detection limit for mannosan and galactosan.

3. Results and discussions

3.1. Median concentrations and interquartile ranges

The medians and interquartile ranges for the PM10 mass, OC, and EC at each of the 7 sites are given in Table 1. As there was a very clear seasonal cycle for the monosaccharide anhydrides, seasonal medians and interquartile ranges are given for these species in Table 2 in addition to the overall (annual) data. Taking EC as a measure for particulate air pollution, it is clear that the urban site of Borgerhout is most polluted, followed by the urban site of Gent and the suburban site of Mechelen. The high EC levels at Borgerhout and Gent are due to the higher traffic density in the vicinity of these sites and the fact that intersections of major highways are within a few km from the sites (Lefebvre et al., 2011). Of the four rural sites, Hamme has the highest EC levels, followed by Lier, Retie, and Houtem. That this last site exhibits the lowest EC levels and also the lowest levels for all other species measured is a consequence of its location within an agricultural region with small population density and little traffic; furthermore, its close distance to the North Sea coast (less than 20 km) and the prevailing westerly winds have the effect that the air is often diluted by fairly clean maritime air.

For the monosaccharide anhydrides (Table 2), the highest levels at each site are noted in winter, followed by autumn, spring, and summer, thus indicating that wood burning is most common in the coldest season of the year. The summer and winter data for Gent can be compared with those of a decade ago for the same city. The average concentration data for Gent in the current study were 320, 40, and 17 ng/m^3 in winter and 18, 2.4, and 1.2 ng/m^3 in summer for levoglucosan, mannosan, and galactosan, respectively. Zdráhal et al. (2002) and Pashynska et al. (2002) obtained winter levels that were about 50% larger, whereas their summer levels were very similar, except for mannosan, for which they obtained about twice higher levels.

3.2. Time series and correlations between the concentration data from the 7 sites

Figs. 3 and 4 show the time series for OC and levoglucosan at the 7 sites. For OC (and also for the PM mass, not shown) the data from the 7 sites are fairly well correlated. At Gent there are 3 samples in a row in July with elevated levels for OC (this was even more obvious in the time series of the PM mass); these samples were taken during the “Ghent City Festival”, the sampling site in Gent was in a small park and some of the Festival activities took place in that park. The concurrent behavior for OC and the PM mass was also seen in the study of Vercauteren et al. (2011), whereby samples were taken in parallel every sixth day over a full year at 6 sites in Flanders. It is in part explained by meteorology, but also the fact that a substantial fraction of the OC and the PM (for the latter, also the secondary inorganic aerosol) is of secondary nature, and thus formed on regional rather than local scales, plays a role. The good correlation for OC is illustrated in Table 3 (the 3 “Ghent City Festival” samples were excluded from the correlation analysis). The site by site correlation coefficients for OC are all larger than 0.9 for 5 of the 7 sites (the exceptions are Hamme and Houtem); the same was seen for the PM mass (not shown). The time series for EC (not shown) showed a much less coherent character and clearly lower correlations (the only correlation coefficient larger than 0.9 was that between Borgerhout and Mechelen). EC in Flanders originates predominantly from traffic and local and line sources (i.e., highways) are the prevailing sources (Lefebvre et al., 2011).

The time series for levoglucosan (Fig. 4) is quite different from that for the OC; as already indicated in Section 3.1, the lowest levoglucosan levels are noted in summer and the highest ones in winter. However, with the exception of the data for Hamme, the levoglucosan data show a concurrent behavior and are highly correlated between the several sites. The peculiar behavior for Hamme has to be attributed to wood burning in several houses nearby the sampling site. The site by site correlation coefficients (r) for levoglucosan are given in Table 4; the levoglucosan data of 5 of the 7 sites (i.e., Retie, Lier, Mechelen, Borgerhout, and Gent) are very highly correlated with each other (all

Table 1
Median concentrations and interquartile ranges (in μg/m^3) over the full year (February 2010–February 2011) for the PM10 mass, OC, and EC at 7 sites in Flanders, Belgium.

	PM	OC	EC
	Median (25%–75%)	Median (25%–75%)	Median (25%–75%)
Borgerhout	23 (18–32)	2.9 (2.0–4.4)	1.30 (0.90–1.87)
Gent	28 (20–35)	3.0 (2.1–4.5)	0.93 (0.67–1.23)
Mechelen	20 (16–31)	3.3 (2.1–4.3)	0.80 (0.49–1.15)
Hamme	26 (19–34)	4.0 (2.9–5.8)	0.63 (0.42–0.82)
Lier	21 (16–29)	2.7 (1.7–4.1)	0.58 (0.40–0.83)
Retie	18 (14–26)	2.5 (1.6–4.0)	0.44 (0.30–0.62)
Houtem	18 (13–27)	1.5 (0.9–2.4)	0.33 (0.22–0.44)

Table 2
Overall (annual) and seasonal median concentrations and interquartiles ranges (in ng/m^3) for the monosaccharide anhydrides at 7 sites in Flanders, Belgium.

	Levoglucosan	Mannosan	Galactosan
	Median (25%–75%)	Median (25%–75%)	Median (25%–75%)
Overall			
Borgerhout	81 (17–183)	11.4 (3.1–28)	5.3 (1.6–10.9)
Gent	69 (22–192)	10.4 (3.4–30)	4.9 (1.3–12.4)
Mechelen	95 (23–260)	13.0 (4.5–37)	5.3 (1.5–14.4)
Hamme	200 (58–514)	34 (10.5–82)	11.3 (3.5–29)
Lier	82 (23–199)	13.8 (3.8–29)	4.9 (1.9–12.0)
Retie	78 (25–167)	11.9 (4.1–28)	4.6 (1.8–10.5)
Houtem	34 (7–112)	5.0 (1.1–15.6)	2.5 (0.7–6.9)
Spring			
Borgerhout	52 (28–87)	8.0 (4.5–13.1)	5.1 (2.1–5.9)
Gent	63 (27–85)	7.7 (4.4–14.0)	4.5 (2.3–6.7)
Mechelen	68 (34–137)	10.6 (6.3–21)	5.5 (3.2–9.5)
Hamme	124 (54–300)	21 (9.4–46)	8.0 (3.8–18.3)
Lier	64 (35–100)	11.6 (5.1–15.4)	4.3 (2.6–7.4)
Retie	52 (28–103)	8.3 (4.4–16.2)	4.7 (2.4–8.0)
Houtem	33 (19–50)	4.2 (2.1–7.9)	3.1 (1.9–4.7)
Summer			
Borgerhout	11.9 (6.7–15.3)	1.56 (1.24–2.3)	0.77 (0.55–1.21)
Gent	14.8 (11.6–22)	2.1 (1.79–3.4)	0.85 (0.71–1.23)
Mechelen	13.8 (7.0–20)	2.2 (1.14–4.0)	0.72 (0.51–1.31)
Hamme	18.1 (13.7–93)	3.2 (2.2–15.6)	0.93 (0.64–4.0)
Lier	13.2 (9.2–22)	2.0 (1.68–3.3)	1.08 (0.62–1.78)
Retie	10.9 (8.5–22)	1.87 (1.36–3.1)	1.29 (0.54–1.85)
Houtem	5.2 (2.8–6.2)	1.05 (0.61–1.16)	0.58 (0.35–0.73)
Autumn			
Borgerhout	167 (90–220)	24 (14.3–36)	7.0 (3.9–10.9)
Gent	168 (93–270)	24 (11.8–42)	8.1 (4.1–13.6)
Mechelen	160 (83–270)	21 (10.2–42)	6.5 (3.7–13.9)
Hamme	340 (193–550)	52 (31–114)	18.7 (9.8–31)
Lier	136 (86–250)	17.7 (11.4–41)	6.2 (3.5–13.1)
Retie	129 (82–189)	20 (11.2–34)	5.5 (3.4–11.8)
Houtem	68 (30–151)	9.5 (4.2–21)	3.1 (1.8–7.2)
Winter			
Borgerhout	300 (130–460)	32 (20–55)	15.0 (8.0–24)
Gent	330 (166–430)	33 (26–54)	14.2 (9.3–22)
Mechelen	330 (184–520)	37 (28–64)	15.9 (12.1–23)
Hamme	640 (460–1010)	88 (69–124)	33 (20–48)
Lier	300 (131–440)	34 (20–61)	15.9 (9.7–23)
Retie	270 (122–390)	31 (20–54)	13.9 (7.7–22)
Houtem	138 (49–260)	17 (8.3–37)	7.6 (3.4–15.5)

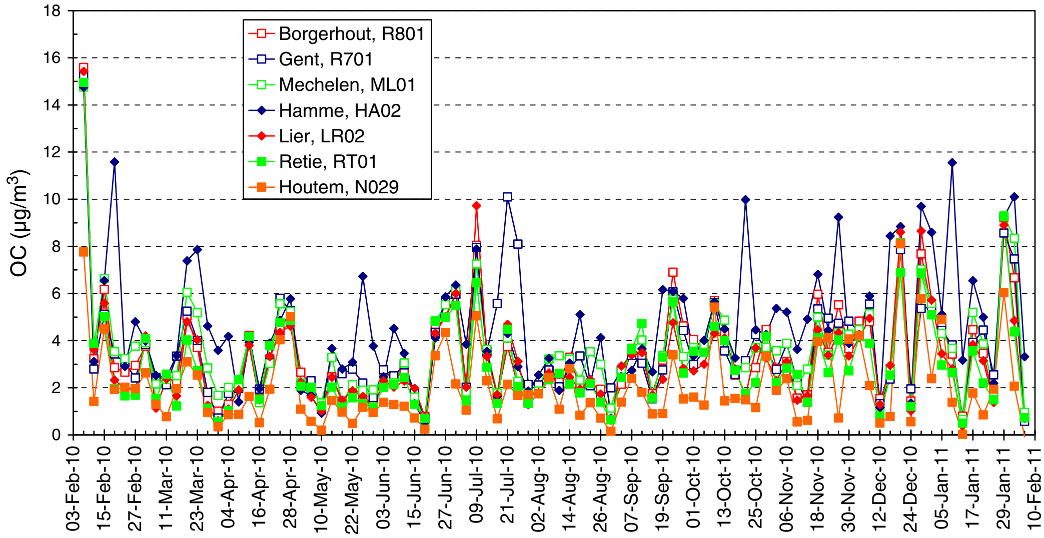

Fig. 3. Time series for PM10 OC at 7 sites in Flanders, Belgium.

r > 0.9, except 0.86 between Retie and Gent). This indicates that wood burning in Flanders is a regional scale phenomenon and that it is probably taking place in many individual houses on similar occasions (e.g., on cold days, weekends or holidays). That the high correlations between the 5 sites are not due to a few (exceptional) concentration data is shown in Fig. 5, which shows the scatterplots between the levoglucosan data of Borgerhout and the 4 other sites. Also given in Fig. 5 are the regression lines (forced through the origin) between the data from Borgerhout and the 4 other sites. It is interesting to note that the slopes of the four regression lines are all close to 1 (they range from 0.92 to 1.14), which is again consistent with a regional phenomenon with many wood burning sources throughout Flanders.

3.3. Correlations among and concentration ratios between the monosaccharide anhydrides; relative importance of softwood and hardwood burning

At each of our 7 sites, the 3 monosaccharide anhydrides levoglucosan, mannosan, and galactosan were very highly correlated with each other. All correlation coefficients were higher than 0.95, except that between levoglucosan and mannosan at Hamme, which was 0.93. Inspection of the various scatter plots indicated that the very good correlations were not due to a few exceptional high concentration data.

The ratio of levoglucosan to mannosan (L/M) has been proposed to distinguish between softwood and hardwood burning and that between levoglucosan and the sum of mannosan and galactosan [L/(M+G)] to differentiate between wood burning and other sources of biomass burning (e.g., Schmidl et al., 2008; Engling et al., 2009; Fabbri et al., 2009; Favez et al., 2010; Piazzalunga et al., 2011). Table 5 gives a selection of ratios that have been reported in the literature for different biomass burning sources.

The annual average L/M ratios for our 7 sampling sites ranged from 6.2 to 7.1 and there was little variation with season; for the winter and summer campaigns at Gent in 1998 and 2000–2001 (Zdráhal et al., 2002; Pashynska et al., 2002) the campaign average L/M ratios were in the range of 4.1–7.2 and thus similar to those obtained in the current study. The annual average L/(M+G) ratios at our 7 sites were in the range of 4.5–4.9, whereas the winter and summer campaign average L/(M+G) ratios for Gent in 1998 and 2000–2001 were 3.4–5.6, and thus also similar to those obtained in the present study. When

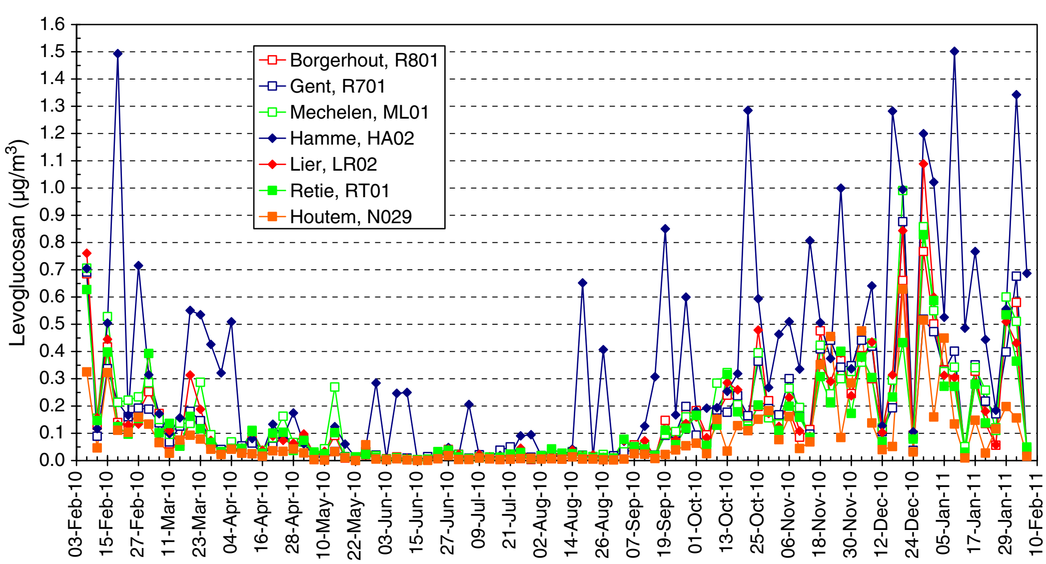

Fig. 4. Time series for PM10 levoglucosan at 7 sites in Flanders, Belgium.

Table 3
Between site correlation coefficients for the PM10 OC concentrations over the full year (February 2010–February 2011) from 7 sites in Flanders, Belgium. The 3 Ghent City Festival samples were excluded from the correlation analysis.

	Retie	Lier	Mechelen	Borgerhout	Hamme	Gent	Houtem
Retie	1						
Lier	0.96	1					
Mechelen	0.94	0.94	1				
Borgerhout	0.96	0.96	0.96	1			
Hamme	0.64	0.68	0.75	0.72	1		
Gent	0.92	0.94	0.95	0.96	0.72	1	
Houtem	0.80	0.82	0.82	0.84	0.55	0.82	1

comparing the ratios in Table 5 with those for our aerosol samples, it can be concluded that lignite could only provide a small contribution to the levels of the monosaccharide anhydrides in PM10 in Flanders. Anyway, lignite is not really used as a fuel in Flanders. Based on the ratios, peat and bituminous coal could in principle be contributors, but peat is not used as a fuel in Flanders either. According to Van Steertegem (2012), the energy use in households in Flanders in 2010 came mainly from oil and natural gas, while biomass (wood) and coal were much less and about equally important. However, anthracite and not bituminous coal is the coal type used in households. Moreover, bituminous coal burning does not yield very large emissions of levoglucosan; the levoglucosan/OC ratio in the emissions is only 0.0124 (Kourtchev et al., 2011), which is about an order of magnitude lower than in the emissions of wood burning. It may therefore be concluded that the monosaccharides in PM10 in Flanders are essentially due to wood smoke. When comparing our aerosol ratios with those from hardwood and softwood burnings, it can be concluded that the latter was more important than the former in Flanders in 2010–2011 and that this was also the case at Gent in 1998 and 2000–2001.

Based on data that were obtained for the combustion of common hardwoods (beech and oak) and softwoods (spruce and larch) in wood stoves in Austria, Schmidl et al. (2008) derived the following equation for obtaining the % of spruce burned (relative to the % of hardwood):

$$\%\text{spruce} = \left(14.8 - R_{L/M}\right)/0.112 \quad (1)$$

where $R_{L/M}$ is the ratio of the levoglucosan to mannosan concentrations in the ambient air. If we assume that the Austrian approach is also transferable to Flanders and apply Eq. (1) to our data, we obtain an annual average % spruce and associated standard deviation of 71 ± 14% for our 7 sites (based on 633 samples; mannosan was below detection limit in 11 samples). The annual averages of the 7 individual sites differed little from each other; they ranged from 68 to 77%. There was also little variation in the % spruce data with season; the seasonal average % spruce data for our 7 sites ranged from 65 to 87% and there was no evidence of a seasonal cycle. By making use of Eq. (1) in their study on the impact of wood burning in three Austrian regions, Caseiro et al. (2009) estimated that the spruce contribution in the biofuel mix burned was in the range of 75–95% for the months January, February, and December. These data are similar to ours, but suggest that softwood burning is slightly more important in the three Austrian regions than in Flanders. In their study at 6 sites in Lombardy, Italy, Piazzalunga et al. (2011) obtained an average L/M ratio of 6.8 in the alpine town of Sondrio, where the local availability of softwood is the highest, but higher ratios for the sites located in the plain (i.e., 10 in Lodi and 13.6 in Mantova). The L/M ratio at Sondrio is similar to ours, but those at Lodi and Mantova are clearly higher, suggesting a relatively larger contribution from hardwood burning at the latter sites. When making use of Eq. (1) to derive the % spruce, we obtain percentages of 71, 43, and 10.7% for Sondrio, Lodi, and Mantova, respectively. Favez et al. (2010) measured levoglucosan and mannosan in PM2.5 samples, which were collected from 14 to 29 January 2009 at an urban station in the Alpine city of Grenoble, France, and they obtained a mean L/M ratio of 10.6; by making use of two different composite wood burning profiles, they arrived at contributions from beech smoke of 89% and 94%. Favez et al. (2010) concluded that this result makes sense with the assumption of the prevalence of hardwood combustion in French cities; however, they provided no arguments or data for substantiating their assumption. Besides monosaccaharide anhydrides, also other organic aerosol species, such as syringol and its derivatives, guaiacol and its derivatives, and retene, can be used to differentiate between hardwood and softwood burning (e.g., Bari et al., 2009). These authors measured a number of those other tracer species in PM10 samples, which had been collected from November 2005 to March 2006 in the residential town Dettenhausen surrounded by forests near Stuttgart in southern Germany. They found that hardwood burning was clearly more

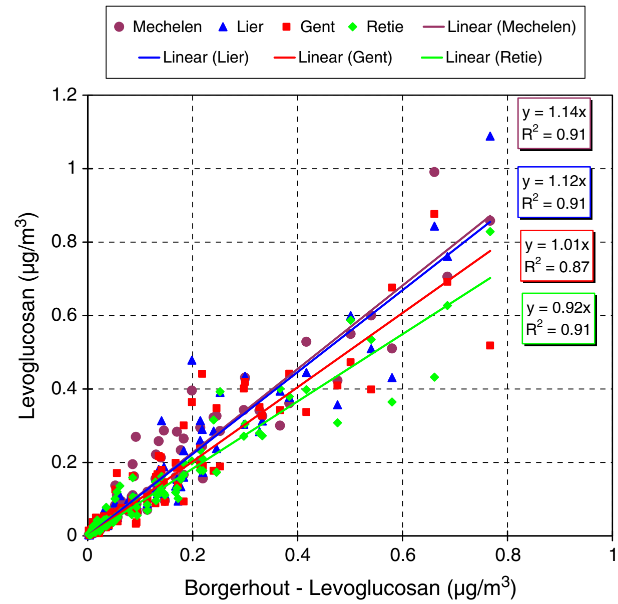

Fig. 5. Scatterplots of the levoglucosan data of 4 sites versus the levoglucosan data of Borgerhout.

Table 4
Between site correlation coefficients for the PM10 levoglucosan concentrations over the full year (February 2010–February 2011) from 7 sites in Flanders, Belgium.

	Retie	Lier	Mechelen	Borgerhout	Hamme	Gent	Houtem
Retie	1						
Lier	0.96	1					
Mechelen	0.92	0.96	1				
Borgerhout	0.96	0.95	0.96	1			
Hamme	0.61	0.62	0.62	0.65	1		
Gent	0.86	0.90	0.93	0.94	0.67	1	
Houtem	0.76	0.81	0.82	0.82	0.47	0.85	1

Table 5
Ratios of levoglucosan to mannosan (L/M) and of levoglucosan to the sum of mannosan and galactosan [L/(M + G)] for different biomass burning sources.

Sample type	L/M	L/(M + G)	Data source
Miocene lignite	54	54	Fabbri et al. (2009)
Peat	8.6	4.9	Kourtchev et al. (2011)
Bituminous coal	3.1	2.5	Kourtchev et al. (2011)
U.S. woods, fireplaces			Fine et al. (2004)
Hardwoods	13–24		
Softwoods	3.9–6.7		
Austrian wood stoves			Schmidl et al. (2008)
Hardwoods	14–15	8.5–9.9	
Softwoods	3.6–3.9	1.2–2.8	

important than softwood burning in their samples. It is difficult to assess the uncertainty that is associated with our large % spruce contribution for Flanders; one may wonder to what extent the Austrian wood stove data of Schmidl et al. (2008) are applicable to wood burning in domestic wood stoves and fireplaces in Flanders. Data on the various types of wood burned in Flanders are currently not available, but would help in this respect. Also measurements of other wood burning indicators besides the monosaccharide anhydrides would be of value.

3.4. Contribution from wood burning to the PM10 OC and the PM10 mass

Several conversion factors have been used in the literature to convert the levoglucosan concentration into contributions from wood burning to the OC or the PM mass. For their PM10 samples collected at Gent in 1999, Zdráhal et al. (2002) made use of the ratio of 100 ± 40 mg of levoglucosan/g of OC, which was obtained by Fine et al. (2001) for fine particle (PM2.5) emissions from fireplace combustion of woods in the northeastern United States. That ratio corresponds to a levoglucosan to wood smoke OC conversion factor of 10. Puxbaum et al. (2007) gave an overview of various conversion factors and noted that the factor is quite variable for different burning conditions and wood types. They reported that for U.S. stoves and fire places, a factor of 7.35 (Fine et al., 2002) is used and on the basis of data derived in Austria from test burns of wood common for alpine environments a factor of 7.1 could be deduced, which is quite close to the U.S. value. For 5 of their 6 background sites along a west–east transect in Europe, Puxbaum et al. (2007) decided to use a levoglucosan to wood smoke OC conversion factor of 7.35, whereas the factor was 6 for the site of Aveiro; they estimated that the uncertainty that was associated with their factors was either 15% or 30%, depending upon the site. In their study on the composition of wood smoke from Austrian wood stoves Schmidl et al. (2008) state that the OC fraction accounts for around 52 ± 4% of the particle mass for all the wood types as pieces and that the mix of wood, as used in Austrian wood stoves, yields wood smoke that contains 9.3% levoglucosan. By dividing the 52% for OC by the 9.3% for levoglucosan, we arrive at a levoglucosan to wood smoke OC conversion factor of 5.59 to obtain the OC concentration from wood smoke for Austrian wood stoves. As to the factor to convert the levoglucosan concentration into PM10 mass from wood smoke, Schmidl et al. (2008) suggest to use a value of 10.7. The latter factor was also adopted by Caseiro et al. (2009) in their study on the impact from wood burning in three Austrian regions. As conversion factor from levoglucosan to OC from wood burning, Caseiro et al. (2009) used a value of 6.1 and they estimated that the uncertainty in this factor is not higher than −15% to +35%. Although the factor of 6.1 was also based on the experiments of Schmidl et al. (2008), it is 10% larger than the value of 5.59 that was derived by us. Considering that our % spruce data are similar to those found in Austria (see Section 3.3), we assume that the Austrian conversion factors may also be appropriate for Flanders. We therefore decided to multiply our levoglucosan data by factors of 5.59 and 10.7 to obtain respectively the OC and PM from wood burning in PM10 in Flanders. Considering the various uncertainties involved, we estimate that the uncertainty that is associated with our wood smoke OC and PM mass contributions is around 30%.

Figs. 6 and 7 show the time series of the percentages OC and PM10 mass from wood burning at our 7 sites. The pattern in both figures is fairly similar to that observed in Fig. 4 for the time series of levoglucosan. The patterns for Hamme in both Figs. 6 and 7 are as in the case of Fig. 4 quite peculiar and differ substantially from the patterns for the other 6 sites. The patterns for Hamme clearly illustrate the important impact from local wood burning nearby our sampling site on the OC and PM10 mass levels at this site. The percentage contributions from wood burning to the OC and the PM10 mass in Figs. 6 and 7 show a clear seasonal character, with highest contributions in winter and lowest ones in summer. Furthermore, for 6 of our 7 sites, the time series show a concurrent behavior. As a consequence of the similarities of the patterns in Figs. 6 and 7 with the pattern in Fig. 4, the between site correlation coefficients for the percentages of OC and PM10 mass from wood burning were fairly similar to the between site correlation coefficients for levoglucosan.

Table 6 gives the annual and seasonal averages and associated standard deviations for the percentage contributions from wood burning to the PM10 OC and PM10 mass and for the PM10 mass concentrations from wood burning. For the 3 types of means given in Table 6, the values are at each site largest in winter, followed by autumn, spring, and summer. The means for Hamme are for each type of averages larger than those for the other sites, again indicating the large impact from very local wood burning at this site. The difference between Hamme and the other sites is much larger in summer than in the other seasons, suggesting that wood burning at this site may also be used for other purposes (possibly cooking) than is the case on a regional scale in Flanders. The seasonal means of our other 6 sites are quite similar to each other. At Houtem, somewhat lower means are observed for the

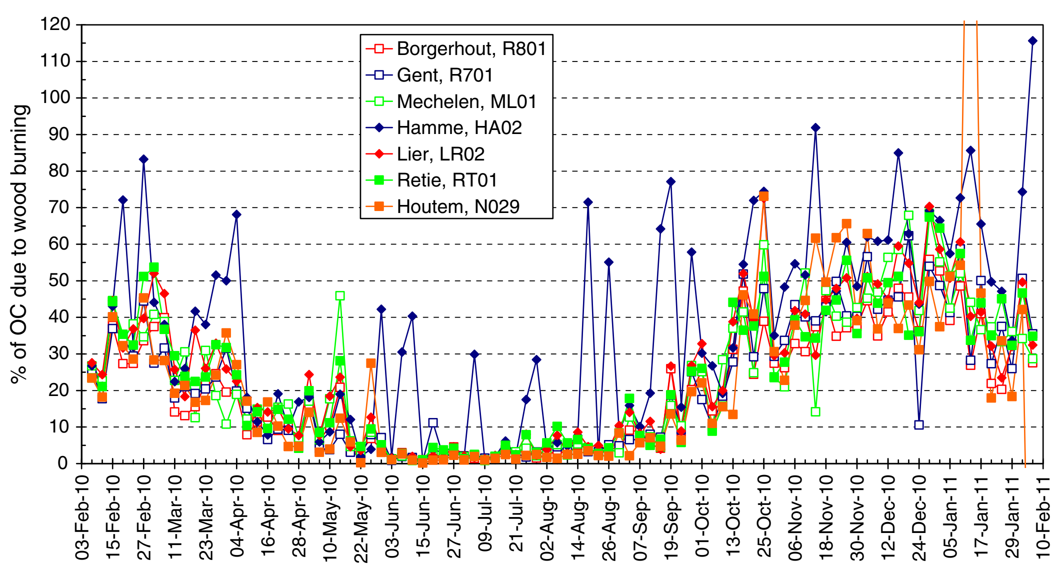

Fig. 6. Time series of the % contribution from wood burning to the PM10 OC at 7 sites in Flanders, Belgium.

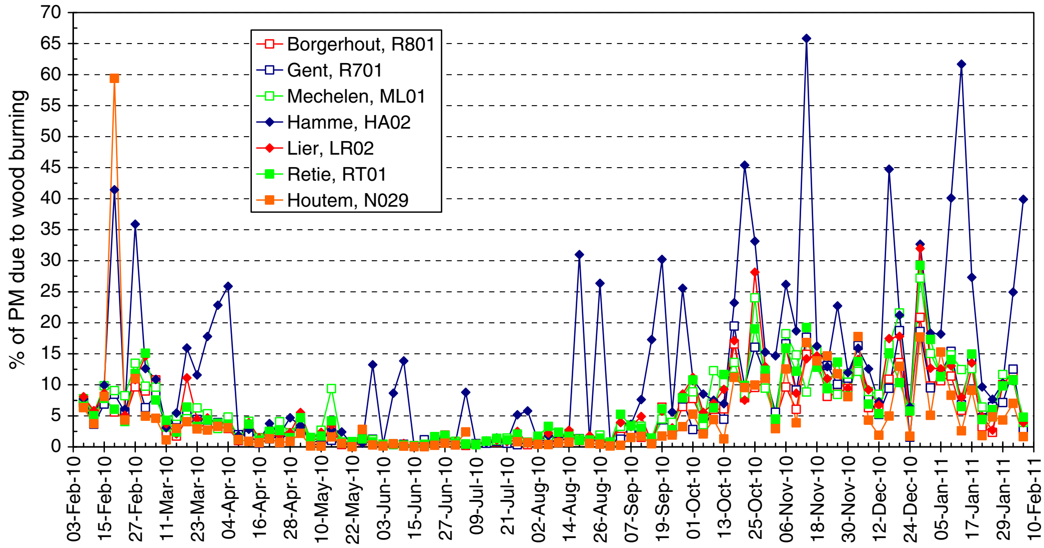

Fig. 7. Time series of the % contribution from wood burning to the PM10 mass at 7 sites in Flanders, Belgium.

PM10 mass concentration from wood burning than at the other sites, though, which is likely due to the dilution of the air at this latter site by clean maritime air, as was indicated above. The Gent summer and winter averages for the % contribution from wood burning to the OC of Table 6 are very similar to those based on the 1998 and 2000–2001 data for Gent from Zdráhal et al. (2002) and Pashynska et al. (2002), as given in the Introduction above. However, for the old data a levoglucosan to OC wood burning conversion factor of 10 was used, whereas the conversion factor for the data of the current study was 5.59. If this new conversion factor is used with the old data, then the % OC from wood burning becomes almost a factor of two lower than is given in the Introduction. This might suggest that the contribution from wood burning to the OC at Gent has nearly doubled over the past decade. However, one should be careful with such conclusion; in both Zdráhal et al. (2002) and Pashynska et al. (2002), at most 10 daily samples were taken per summer or winter campaign, whereas the number of samples at each site in each season was 24 in the current study. Also, the site at Gent in the current study was near the center of the city whereas it was at the outskirts of the city in the old studies. This difference in sites is not expected to have a large effect, though; as indicated above, the data for the other sites of the current study (with the exception of Hamme and to a lesser extent Houtem) are all very similar to those for Gent.

Our data of Table 6 can also be compared with the results from studies in other European countries, whereby levoglucosan was used as wood burning tracer. Puxbaum et al. (2007) studied the contribution from wood burning organic matter (estimated as 1.4 * wood burning OC) to the PM2.5 organic matter (estimated as 1.7 * OC) from mid-2002 to mid-2004 at 7 background sites along a west–east transect in Europe, extending from the Atlantic (Azores) to the mid-European background site KPZ (K-Puszta, Hungary). The relative contributions of biomass smoke to organic matter (OM) ranged from around 9 to 11% at the three elevated sites, as well as for the Azores, to 36% at the low-level site Aveiro (Portugal) and 28% at KPZ. Biomass smoke provided summer contributions to the OM of around 1–6% at the mid and west European background sites and winter contributions of around 20% at the elevated mountain sites and 47–68% at the rural flat terrain sites Aveiro and KPZ, not including secondary organic aerosol from biomass combustion sources. Although our data in Table 6 give percentages of wood burning OC to the total OC in PM10, there is good agreement between the data of the rural flat terrain sites of Puxbaum et al. (2007) and our data. Yttri et al. (2005, 2009) determined the contribution from wood burning to the PM10 OC and PM10 mass during campaigns in 2001 and 2002 at a kerbside and urban background site in Oslo and at a suburban site 120 km NE of Oslo. Their average contributions from wood burning to the PM10 OC were 15% for the Oslo kerbside (autumn campaign), 30% for the Oslo urban background site (winter campaign) and 11% and 100% for the summer and winter campaigns, respectively, at the suburban site. The data for the Oslo sites are on the low side when compared to our data in Table 6, whereas those for the suburban site are rather similar to our data for Hamme. Caseiro et al. (2009) conducted a study at traffic and background sites in three Austrian regions, i.e., Vienna, Graz, and Salzburg. They provided overall and seasonal data for the % OC and the % PM10 mass from wood burning and for the PM10 mass from wood burning. The data for their Viennese sites are similar to those of our 6 regionally influenced sites mentioned above, while those for their sites in Graz and to a lesser extent Salzburg resemble our data for Hamme. For example, their annual averages for the % OC from wood burning are in the range of 18–22, 23–38, and 22–38% in Vienna, Graz, and Salzburg, respectively, whereas our annual averages (see Table 6) are in the range of 20–25% for 6 of our 7 sites and 36% at Hamme. As another example, the PM10 mass concentrations from wood burning are in the range of 1.3–1.7, 2.7–5.2, and 1.7–2.3 μg/m^3 in Vienna, Graz, and Salzburg, respectively, whereas our annual averages (Table 6) are in the range of 1.4–1.8 μg/m^3 for 5 of our 7 sites and 3.8 μg/m^3 at Hamme. Similarly as in the current study, Caseiro et al. (2009) also found a clear seasonal cycle for the wood burning data, with highest values in winter and lowest values in summer. Kourtchev et al. (2011) collected PM2.5 samples at Cork Harbour, Ireland, during summer, autumn, late autumn, and winter, 2008–2009 and analyzed the samples for polar organic compounds that are useful markers for aerosol source characterization. The contribution of domestic solid fuel (DSF) burning to the measured OC mass concentration was estimated at 10.8, 50, 66.4 and 74.9% for summer, autumn, late autumn, and winter periods, respectively, based on factors derived from a series of burning experiments on locally available fuels. These percentages resemble our percentages for Hamme, but are higher than the percentages at our 6 other sites. It should be noted that DSF burning in the study of Kourtchev et al. (2011) includes the combustion of peat and bituminous coal in addition to wood burning. Favez et al. (2010) used three different approaches to determine the contribution from wood burning to the PM2.5 OM during 2009 winter at an urban background site in Grenoble, France. One of the approaches used was chemical mass balance (CMB), whereby the wood burning source profile included levoglucosan in addition to a number of n-alkane and polycyclic

Table 6
Overall (annual) and seasonal means and associated standard deviations for the % contribution from wood burning (WB) to the PM10 OC and the PM10 mass and for the PM10 mass concentration (in μg/m^3) from wood burning.

	% contr. from WB to the PM10 OC mean ± s.d.	% contr. from WB to the PM10 mass mean ± s.d.	PM10 mass from WB (μg/m^3) mean ± s.d.
Overall			
Borgerhout	20 ± 16	4.8 ± 4.6	1.5 ± 1.8
Gent	21 ± 18	5.3 ± 5.3	1.6 ± 1.9
Mechelen	23 ± 19	6.3 ± 5.8	1.8 ± 2.1
Hamme	36 ± 27	13.3 ± 14.0	3.8 ± 4.0
Lier	25 ± 19	6.2 ± 6.2	1.7 ± 2.1
Retie	23 ± 18	5.9 ± 5.6	1.4 ± 1.7
Houtem	22 ± 32	4.8 ± 7.5	0.9 ± 1.4
Spring			
Borgerhout	15 ± 10	2.8 ± 2.5	0.73 ± 0.64
Gent	14 ± 9	2.7 ± 2.2	0.74 ± 0.57
Mechelen	18 ± 12	3.8 ± 2.8	1.05 ± 0.91
Hamme	25 ± 18	7.3 ± 7.6	1.98 ± 1.88
Lier	20 ± 13	3.5 ± 3.5	0.94 ± 1.00
Retie	19 ± 12	3.4 ± 3.1	0.84 ± 0.87
Houtem	15 ± 10	1.9 ± 1.5	0.42 ± 0.35
Summer			
Borgerhout	2.6 ± 1.3	0.71 ± 0.44	0.14 ± 0.10
Gent	3.3 ± 2.2	0.74 ± 0.38	0.19 ± 0.12
Mechelen	2.8 ± 1.3	0.95 ± 0.57	0.16 ± 0.09
Hamme	14.5 ± 19.3	5.0 ± 8.3	1.04 ± 1.71
Lier	3.8 ± 2.6	1.03 ± 0.73	0.18 ± 0.13
Retie	3.9 ± 2.6	1.14 ± 0.79	0.17 ± 0.12
Houtem	2.0 ± 1.6	0.51 ± 0.53	0.06 ± 0.04
Autumn			
Borgerhout	26 ± 13	7.2 ± 4.2	1.8 ± 1.1
Gent	28 ± 15	8.4 ± 5.7	2.0 ± 1.4
Mechelen	27 ± 16	9.1 ± 5.6	2.0 ± 1.3
Hamme	46 ± 22	18.9 ± 14.6	4.6 ± 3.4
Lier	32 ± 17	9.5 ± 6.0	1.9 ± 1.3
Retie	28 ± 15	9.2 ± 5.1	1.6 ± 1.0
Houtem	30 ± 22	6.5 ± 5.3	1.2 ± 1.2
Winter			
Borgerhout	36 ± 11	8.6 ± 4.3	3.3 ± 2.4
Gent	40 ± 13	9.2 ± 4.9	3.4 ± 2.4
Mechelen	43 ± 12	11.3 ± 5.4	3.9 ± 2.7
Hamme	60 ± 22	21.9 ± 15.8	7.5 ± 4.7
Lier	43 ± 12	10.6 ± 6.3	3.6 ± 3.0
Retie	43 ± 12	9.9 ± 5.8	3.0 ± 2.3
Houtem	40 ± 53	9.3 ± 12.0	2.0 ± 1.9

aromatic hydrocarbon (PAH) wood burning tracers. Using CMB they found that wood burning accounted for 68% to the OM. This result is similar to our winter percentage of wood burning to the PM10 OC in Hamme. It should be noted that the OC-to-OM conversion factors for wood burning OC and total OC, as used by Favez et al. (2010), were very similar to each other, i.e., 1.7 and 1.78, respectively. Piazzalunga et al. (2011) made use of two different approaches to determine the contribution from wood burning to the PM10 OC and the PM10 mass during winter campaigns at 5 urban background sites and 1 rural site in Lombardy, Italy. The two approaches consisted, on the one hand, of making use of weighted emission factors, based on data of Schmidl et al. (2008), but taking into account the percentage of wood types felled in Lombardy, and on the other hand, positive matrix factorization (PMF). Using the weighted emission factor approach, Piazzalunga et al. (2011) found that about 30% of the OC is attributable to wood burning at their sites; this percentage compares well with the winter percentages of around 40% for 6 of our 7 sites. As to the contribution from wood burning to the PM10 mass, using the same approach, Piazzalunga et al. (2011) found percentages in the range of 5–15% for the 4 southern of their 6 sites and in the range of 11–24% for the 2 northern sites. These percentages are larger than the winter data for our sites, which range from 2.0 to 3.9% for 6 of our sites and is 7.5% for Hamme, thus indicating that wood burning provides a lower contribution to the PM10 mass in winter in Flanders than it does in Lombardy.

Table 7
Effect of a "virtual" subtraction of wood burning (WB) on the number of exceedances of the EU daily PM10 mass limit of 50 μg/m^3.

	Number of exceedances with contribution from WB included	Number of exceedances with contribution from WB excluded	Difference: WB included − WB excluded
Borgerhout	7	3	4
Gent	10	7	3
Mechelen	5	2	3
Hamme	7	2	5
Lier	7	3	4
Retie	3	3	0
Houtem	4	3	1
All sites	43	23	20

3.5. Role of wood burning in the exceedances of the EU daily PM10 mass limit

From the routine data of the VMM measuring network it appears that on a yearly basis, about two thirds of the exceedances of the EU daily PM10 mass limit of 50 μg/m^3 occur in the period October–March. As the contribution from wood burning to the PM10 mass concentration is also largest in those months, it was estimated what the effect of the absence of wood burning would mean for the number of exceedance days (Table 7). For the total of 644 measurement days in the current study, the number of exceedances is reduced from 43 to 23 in the absence of wood burning. In Hamme, where the contribution from wood burning is largest, the largest effect is seen of the "virtual" subtraction of wood burning. However, one has to be careful in interpreting these data. It is often the case that there are several days with a PM10 mass concentration just above 50 μg/m^3. The subtraction of a small contribution may therefore have a pronounced effect on the number of exceedances of the daily PM10 mass limit. Furthermore, the number of exceedances (between 10 and 3 per site) and the number of samples collected (one every 4 days) were too small to allow extrapolation to an entire year. What we wanted to show with our calculations is that the effect of wood burning on the exceedances of the daily PM10 mass limit, because of the seasonal character, is larger than one would expect on the basis of the annual mean PM10 mass contributions from wood burning, which are in the range of 0.9–3.8 μg/m^3 (Table 6). On the 43 exceedance days, the PM10 mass contribution from wood burning was in fact 6 μg/m^3 on average. Our data show that a reduction of wood burning on smog days would be quite effective in reducing peak concentrations. In the U.S. several systems are available that all work on a more or less comparable basis: when model calculations indicate poor air quality in winter, restrictions or even a complete ban are enforced for residential wood burning (http://www.sparetheair.org/Stay-Informed/Particulate-Matter/Wood-Smoke/Regulation.aspx; http://www.valleyair.org/aqinfo/WoodBurnpage.htm; http://www.cabq.gov/airquality/noburn.html). Generally, an exception is made for persons of the lower social classes or for persons with wood burning as the sole source of heating. Besides, such short-time measures are always accompanied by long-term measures, including more rigid regulations for wood burning installations and premiums on the replacement of polluting installations.

4. Conclusions

In our 2010–2011 study on the impact of wood burning in Flanders, use was made of levoglucosan as wood burning indicator and wood burning profiles of Schmidl et al. (2008). The 2010–2011 study confirmed the limited data sets that were obtained over a decade ago for

Gent by Zdráhal et al. (2002) and Pashynska et al. (2002). It appeared that the impact in Gent in 2010–2011 may even have been larger than over a decade ago, although one should be careful in drawing such a conclusion considering the limited number of samples in the earlier studies. The current large-scale study, which involved 24-hour PM10 samplings in parallel every fourth day at 7 sites throughout Flanders over a full year, indicated that the impact from wood burning at all sites showed a clear seasonal variation, with largest wood burning levels in winter, followed by autumn, spring, and summer. A similar seasonality was also observed in various other countries in Europe. Besides, Zdráhal et al. (2002) and Pashynska et al. (2002) also found much higher levoglucosan levels in winter than in summer. It appeared that the levoglucosan levels for 5 of our 7 sites were very highly correlated with each other; all between-site correlation coefficients for the 5 sites were larger than 0.9, except for one which was still 0.86. Moreover, the slopes of the regression lines forced through the origin between the levoglucosan data of the most polluted site (i.e., Borgerhout) and the 4 other sites were all close to 1 (ranging from 0.92 to 1.14). This indicates that wood burning in Flanders is a regional scale phenomenon and that it is taking place in many individual houses on similar occasions (e.g., on cold days, weekends or holidays). The correlation coefficients between the levoglucosan data of the most westerly site (i.e., Houtem, which is at less than 20 km from the North Sea coast) and the data of the 5 sites with very high correlation coefficients were still high (around 0.8), whereas the slope of the regression line of the Houtem levoglucosan data on the Borgerhout data was 0.62. The lower correlation coefficients and lower slope for Houtem are explained by dilution of the air at this site by fairly clean maritime air, taking into account the prevailing westerly winds in Flanders. One site, i.e., Hamme, showed a peculiar levoglucosan time series, with on many occasions very high levels; the correlations with the data from the other sites were only around 0.6. The peculiar behavior for Hamme is attributed to the fact that there is wood burning going on in several houses nearby this site, a fact which was known at the start of our study.

Besides levoglucosan (L), also two other wood burning markers, i.e., mannosan (M) and galactosan (G) were measured in all samples. The L/M and L/(M + G) ratios were used to differentiate between various sources of biomass burning and in particular between softwood and hardwood burning. It was found that softwood burning dominated at our 7 sites; the contribution from softwood was 71 ± 14% (averaged over all samples) and there was little variation with season or with site. Similar percentages were observed in Austria by Caseiro et al. (2009), but in a winter study in Grenoble, France, only around 10% of softwood was obtained. Our differentiation between softwood and hardwood burning is based on Austrian wood stove data of Schmidl et al. (2008). One may wonder to what extent those Austrian data are applicable to wood burning in domestic wood stoves and fireplaces in Flanders. Data on the various types of wood burned in Flanders are currently not available, but would help in this respect. Also measurements of other wood burning indicators besides the monosaccharide anhydrides would be of value.

Our levoglucosan data were used in combination with the wood burning profiles of Schmidl et al. (2008) to assess the contribution from wood burning to the PM10 OC and the PM10 mass for each individual sample. The uncertainty, which is associated with these assessments, is estimated at 30% relative. The annual average contributions of wood burning OC to the PM10 OC were in the range of 20–25% for 6 of our 7 sites and 36% at Hamme; the averages for summer were 2.0–3.9% for the 6 sites and 14.5% for Hamme; the corresponding data for winter were 36–43% and 60%. As to the contribution from wood burning to the PM10 mass, the annual averages were in the range of 4.8–6.3% for 6 of our 7 sites and 13.3% at Hamme; the averages for summer were 0.51–1.14% for the 6 sites and 5.0% for Hamme; the corresponding data for winter were 8.6–11.3% and 22%. Our finding that wood burning is an important contributor to the PM10 OC and PM10 mass, especially in winter, is in line with the data from various other sites in other European countries. For example, the results for 6 of our 7 sites are similar to those obtained by Caseiro et al. (2009) for the Vienna region, while our data for Hamme resemble the data for the sites in Graz of Caseiro et al. (2009).

Considering that the contribution from wood burning to the PM10 mass levels is largest in winter and that most of the exceedances in Flanders of the EU daily PM10 mass limit of 50 $\mu g/m^3$ limit occur in the cold season, it was estimated what the number of exceedances would be in the absence of wood burning. For the 644 samples of our data set there were 43 samples where the EU limit was exceeded. After "virtual" subtraction of the PM10 mass from wood burning for these samples, the number of samples with PM10 mass exceedance was reduced to almost half. This indicates that more stringent regulations on wood burning in Flanders, in particular in winter, could help in complying with the European air quality legislation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2012.08.015. These data include a Google map of the most important areas described in this article.

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